Wood pitch fixative evaluation by laser particle size analysis

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SUMMARY

Wood pitch deposition onto the surface of papermaking machinery continues to be a costly problem. Fixatives - substances said to attach wood resin to wood fibre - have been used to alleviate wood pitch deposition to varying degrees of success. This paper aims to evaluate to what degree fixatives alter the colloidal wood pitch particle size.

We were able to show how different wood resin fixatives alter the colloidal wood pitch particle size at three different pH values (4.75, 6.85 and 8.06). The fixatives can be divided into two categories, colloid disrupting and colloid stabilising, according to how they change pitch particle size.

KEYWORDS

pitch, particle size distribution, fixatives, laser particle size analyser, colloidal stability

INTRODUCTION

The term "pitch fixative" can be a misnomer, as demonstrated by Wågberg and Ödberg (*1*) and Shetty *et al* (*2*), who showed that the removal of wood resins from the papermaking system by cationic polyelectrolytes can be achieved not necessarily through fixation onto the fibre but also by the formation of small wood resin agglomerates and colloids large enough to be removed from the papermaking process through fibre entrapment. As a result the meaning of "pitch fixative" has changed to: additives that aid in the removal of wood resins from the papermaking system.

Fixatives have been examined in many ways (*3*) and by many people (*4-9*). In order to better understand pitch deposition Allen (*10*) examined colloidal wood resin particle size in relation to its concentration and Garver and Yuan (*11*) examined colloidal stability with some emphasis on particle size. Wågberg and Ödberg (*1*) measured particle size (*13,14*) using static light scattering techniques, made famous by Rayleigh (*15*), and later refined by Fraunhofer (*16*) and then by Mie (*17*). Laser particle size analysis (LPSA) and static laser light scattering (SLLS) are further applications of these earlier theories. With recent advances in charge coupled devices (CCDs) and computer processors, LPSA by SLLS continues to improve (*18,19*). Fluorescent dyes in conjunction with laser pitch particle counters have also been used in pulp and paper research (*20-22*) though with limited success (*23*).

Fixation is not the only way to address the problem of wood resin deposition. Previous work (*12*) has described the control, management and elimination of wood pitch deposition in terms of four approaches; 1) Pulping operations – through removal of extractives prior to the paper machine. 2) Biological - through treatment of the raw and/or processed fibre. 3) Forestry/Agricultural - through selective, alternative and/or genetically modified fibres as well as harvesting and storage techniques of the wood and/or wood chips. 4) Chemical - through dispersant and/or fixation of colloidal and agglomerate pitch. All four of these approaches will need further development in order to minimise problems associated with wood pitch deposition. In addition to the factors associated with these four approaches, there is also the importance of process stability, namely stable pH, temperature and shear, as a shock change in any of these three process parameters is likely to lead to pitch deposition (*4*).

Knowing that different fixatives interact differently with different concentrations of wood extractives (*5,24,25*), the methods of Wågberg and Ödberg (*1*) could be used to further highlight these different interactions. This paper aims to study the effect that a range of different wood pitch fixatives have on the particle size distributions of wood resins and to determine whether fixatives can increase the size of aggregated pitch such that it is entrapped in fibres and/or the fibre mat.

EXPERIMENTAL

Colloidal wood resin

Hydrophobic resinous extractive was extracted from dried thermal mechanical pulp (TMP) of *Pinus radiata* with hexane using Soxhlet apparatus. Most of the hexane was first removed by rotary evaporation at 45°C and the remainder of solvent was blown dry. The "dry" extractives sample was stored at -4°C before being dissolved into a 20 weight percent solution of acetone. The acetone was removed from the wood resin by dialysis (26) in order to prepare the colloidal wood resin. The composition of the extracted wood resin, shown in Table 1, was determined by GC using a method previously described (*26*).

Buffers

Three 20 mM amine buffers were used to control the pH to 8, 6.85 and 4.75. Tris(hydroxymethyl)aminomethane (pKa 8.06) and ethylenediamine (pKa 6.85) were obtained from Aldrich and prepared in distilled water. N,O-dimethylhydroxylamine was obtained by distilling at 100°C the hydrochloride salt with a molar excess of KOH to obtain the free amine with a yield of 82.5%. Each buffer solution was titrated with 1M HCl until the pH of the buffer equalled the pKa of the amine.

Fixatives

A range of fixatives commonly used in the pulp and paper industry were obtained

Table 1.
Composition of extracted wood resin

Component	Composition mg/g
Fatty Acid	46
Resin Acid	103
Triglyceride	42

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Table 2
Physical properties of Fixatives

Label	Chemistry	% Solids	Molar Mass*	Charge Density (meq/g) dry
Fix A	pDADMAC	43	Low	10.3
Fix B	pDADMAC	39	Medium	4.6
Fix C	pDADMAC	21	Medium	9.0
Fix D	cPAM	58	High	0.4
Fix E	cPAM	45	High	1.6
Fix F	cPAM	58	High	2.3
Fix G	Guar gum	100		0
Fix H	p(AM-co-DADMAC)	67	Medium	1.9
Fix I	p(AM-co-DADMAC)	63	Medium	4.1
FixJ	pAC	47	low	3.6
Fix K	Epi-DMA	52	low	10.3
Fix L	PEI	26	Low	8.2
Fix M	PEI	28	low	9.9
FixN	pVAm	35	low	9.3
Fix O	pVAm	17	medium	3.7

* Low MW= $<10^4$, Medium MW= 10^4-10^6, High MW=>10^7

from Norske Skog Boyer who received them for evaluation from various suppliers. The fixatives investigated included poly diallydimethylammonium chloride (pDADMAC), cationic polyacrylamide (cPAM), co-polymer of acrylamide and diallydimethylammonium chloride (p(AM-co-DADMAC), guar gum, poly(aluminium chloride) (pAC), epichlorohydrin-dimethylamine (epi-DMA), polyvinylamines (pVAm) and polyethyleneimine (PEI). The basic properties measured for each fixative investigated is presented in Table 2. The charge density of the fixatives was determined by titration of 10 mL of a 1% solution of fixative (as received) using a Mutek PCD-02 (Particle Charge Detector) to determine the charge neutralisation endpoint. The % solids were determined by drying a sample at 60°C for 48 hours.

Particle size analysis

A 15mL aliquot of the dialysed colloidal wood resin was added to 585 mL of 50°C 0.001M potassium nitrate (*26*), pH adjusted solution. The pH was adjusted using either 0.16M nitric acid or 0.18M potassium hydroxide or one of the amine buffers. This solution was used to fill the centrifugally pumped sample cell of the Micromeritics Saturn DigiSizer 5200® (Micromeritics Instrument Co. USA). Particle size measurements were made through exposures of a solid state 658nm diode laser at ten different angular positions. The 16 mm parallel laser beam was passed through the sample cell, and then to the Fourier lens which projected the light onto a ~1.3 M element CCD. Deconvolution of the data was carried out with Mie (17) theory using a sample refractive index of 1.540/0.0001 and 0.983 density(g/cm^3).

A series of three measurements, each 6 minutes apart, were recorded for a colloidal wood resin sample to establish the average particle size for the colloidal wood resin. Immediately after this set of measurements fixative was added to the sample cell in the Saturn Digisizer 5200 and mixed using the ultrasonic probe in the instrument. Subsequent measurements were then taken 6 minutes apart, this being the measuring time of the instrument.

RESULTS AND DISCUSSION

Figure 1 shows the particle size distribution of the dialysed colloidal wood resin extract at 50°C and at 6.8 pH. This distribution is very similar to that obtained by Wågberg and Ödberg (*1*) even though they made use of TMP from the Ortviken Mill (SCA, Sweden) in which colloids were taken directly from the pulp. In their work they used 5.2 pH, a colloid refractive index of 1.200/0, a colloid specific gravity of 1.0, and a Malvern Mastersizer (Malvern Instruments Ltd, UK).

Figure 2 illustrates how the average particle size of the wood resin colloids increases with the addition of the pDADMAC fixative (FixC). Four levels of fixative addition to the 600 mL colloidal sample were explored (1.88 mg, 3.76 mg, 5.64 mg, 7.52 mg). These levels were based on 0.5, 1.0, 1.5 and 2.0 kg of as- received fixative per oven dried tonne of TMP. Three measurements were taken at each addition level and from these measurements the mean, mode and median were determined. All three measures show that colloidal particle size increases with the addition of pDADMAC.

The increasing particle size shown in Figure 2 was not described by Wågberg and Ödberg (*1*), most likely due to the fact that they evaluated two higher concentrations of fixatives 100 mg/L and 160 mg/L (which would have roughly equalled 3 and 6 kg of as-received fixative per oven dried tonne of TMP).

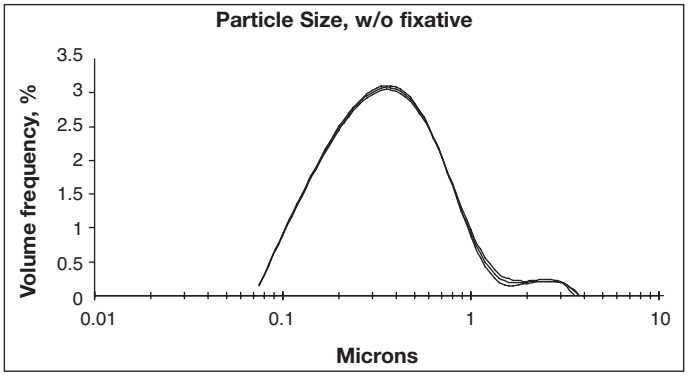
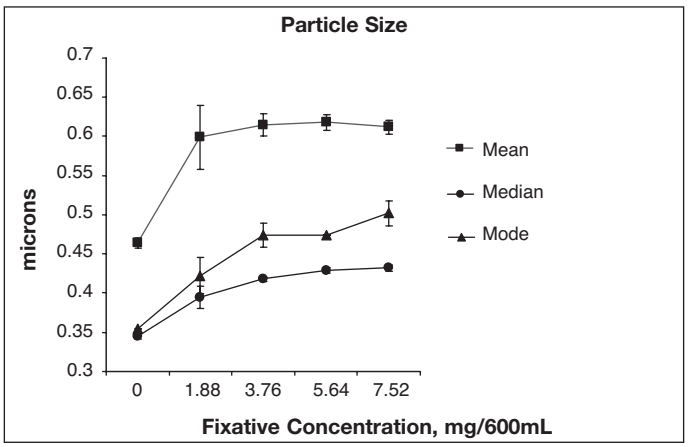


Fig. 1 Colloidal wood (TMP Pinus radiata) resin particle size distributions in microns at 6.8 pH, 50°C.



ig. 2 Colloidal wood (TMP *Pinus radiata*) resin mean, median and mode particle size in microns at 6.8 pH, 50°C over a range of pDADMAC concentrations. (error bars indicate +/- 1 std. dev.)

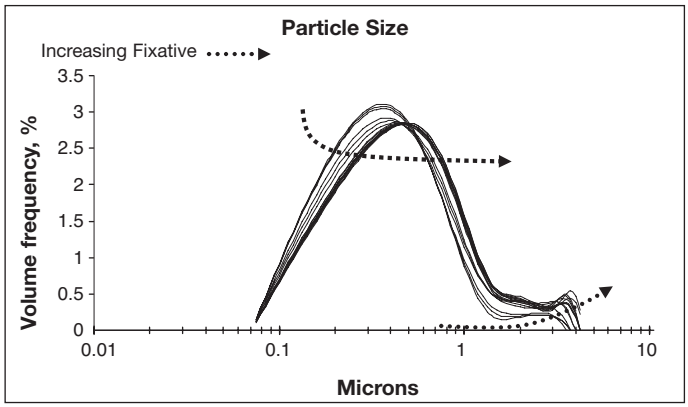


Fig. 3 Colloidal wood (TMP *Pinus radiata*) resin particle size distributions in microns at 6.8 pH, 50°C over an increasing range (0-7.52 mg/600 mL) of pDADMAC concentrations.

Figure 3 shows that the ~0.35 µm particles aggregated towards the ~3.76 µm sized particles with increased pDADMAC fixative addition. Wågberg and Ödberg (*1*) showed that 'small' 0.1-0.4 µm resin particles increased to 'larger' stable 1-10 µm sized particles, which agrees with our findings.

A range of fixatives of varying chemical structure and at different pH levels were investigated. A single addition of fixative was added to the Micromeritics Saturn DigiSizer 5200® sample cell (7.58 mg corresponding to 2 kg/tonne fixative addition). The change in particle size was measured after 6, 12 and 18 minutes. The change in particle size of the "small" wood resin colloids and the "larger" wood resin aggregates over time were determined as shown in Figure 4 and are expressed as m_s and m_l.

The results from the growth of large and small wood resin particles at 4.75 pH are presented in Figure 5. This pH represents a pH common to acid papermaking and a pH below the pK_a of both resin and fatty acids found in softwood extractives.

FixD (pAM) was found to have the fastest growth in large particles at 4.75 pH and at the same time the colloids were found to decrease in size indicating that components in the colloids are removed during the growth of the larger particles. The shift in particles from small colloidal to larger particle size suggest that the new, smaller, colloids are more thermodynamically stable than the initial colloids. FixE, also a pAM, has both rapid growth in colloidal and larger particle size. The higher charge of FixE compared with FixD may be driving the removal of dissolved (i.e. <0.1 µm) extractive components from solution and their incorporation into more structured particles. This trend does not occur with FixF which is another pAM of higher cationic charge and molar mass. This suggests that there is an optimum cationic charge for the removal of extractives from solution. In examining the results of the pAMs (FixD, FixE & FixF)

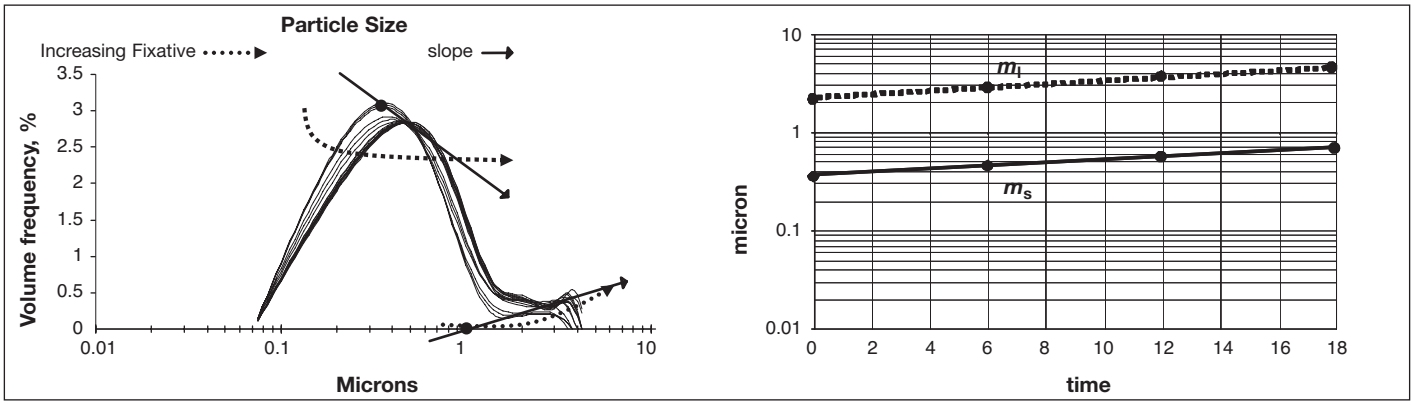


Fig. 4 Determination of m_s and m_l from the change in size with time of "small" wood resin colloids (m_s) and change in size with time of "larger"agglomerating particles (m_l).

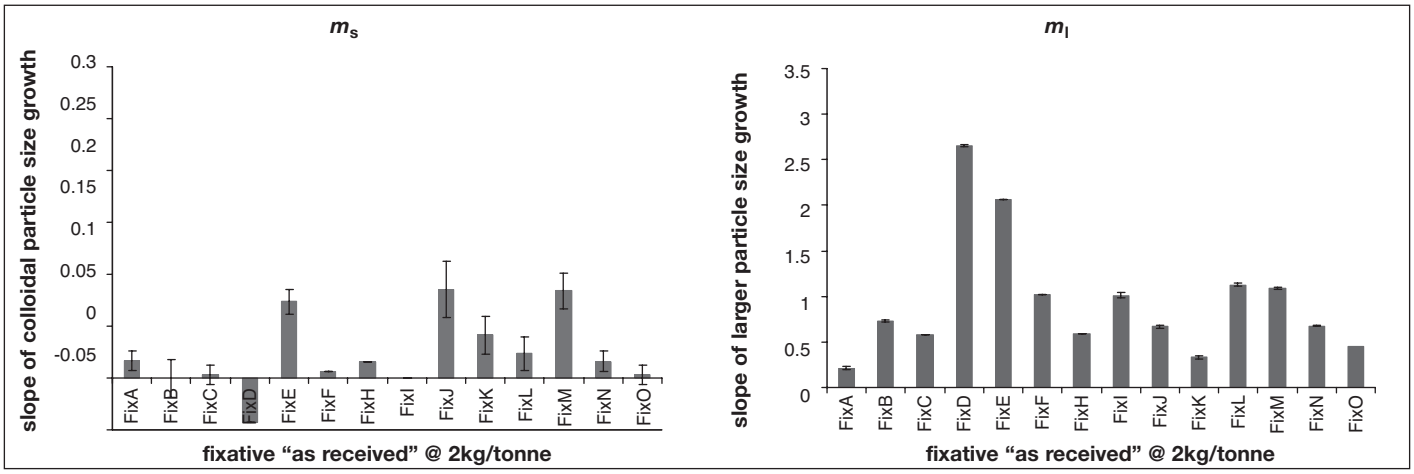


Fig. 5 Change in particle size of wood resin with fixative addition (2kg/tonne as received) at 4.75 pH

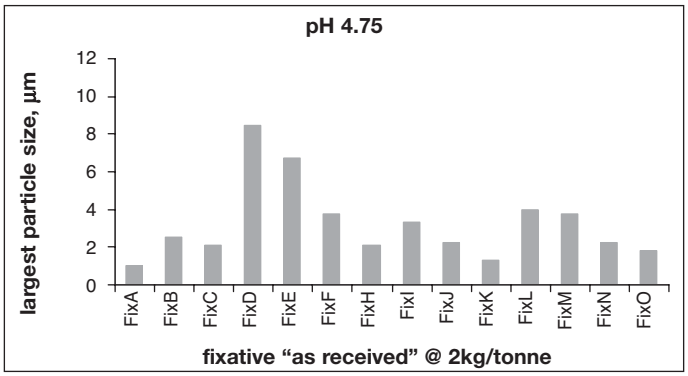


Fig. 6 Largest particle size (µm) at 4.75 pH.

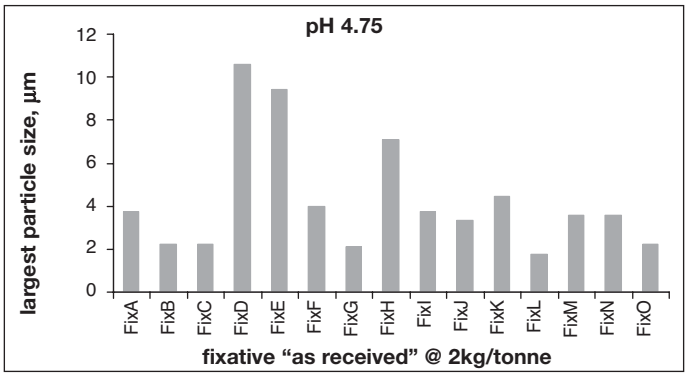


Fig. 8 Largest particle size (µm) at 6.85 pH.

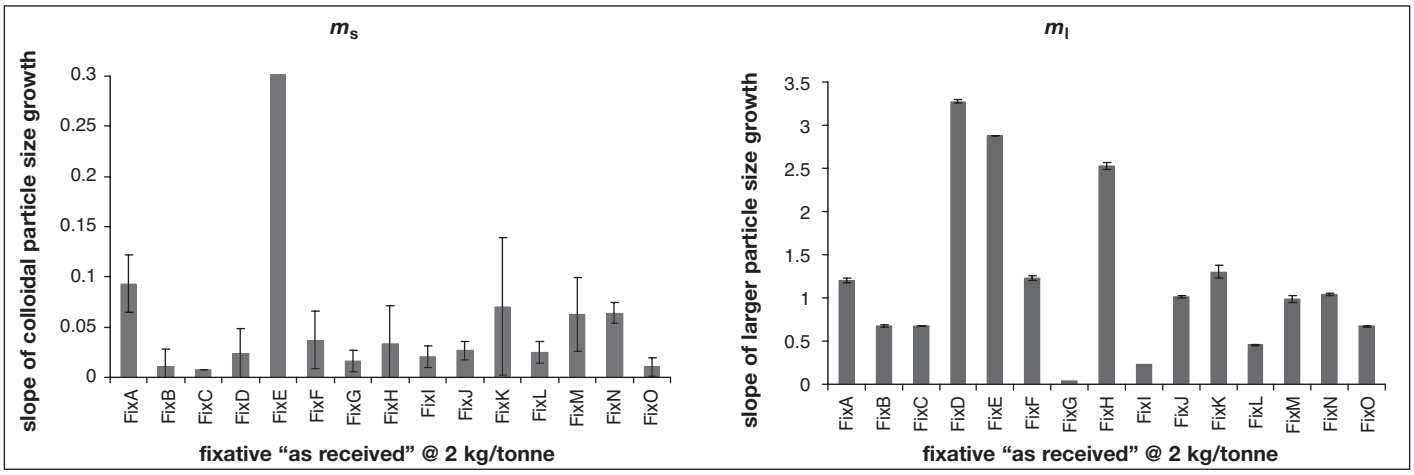


Fig. 7 Change in particle size of wood resin at fixative additions (2 kg/tonne) at 6.85 pH.

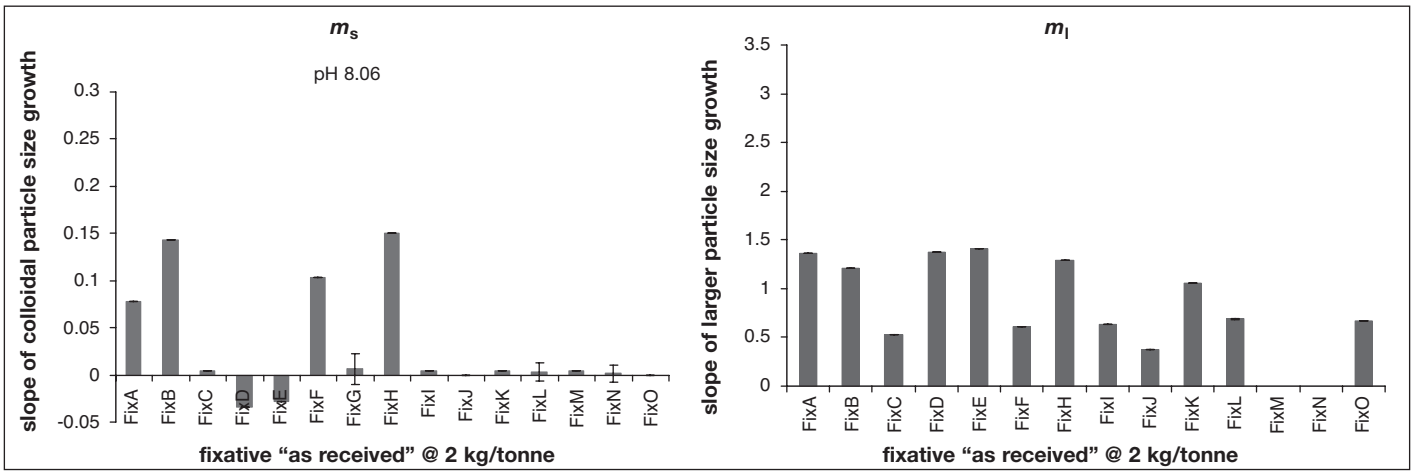


Fig. 9 Change in particle size of wood resin with fixative addition (2kg/tonne) at 8.06 pH

it should be noted that they are 2-4 orders of magnitude larger in molar mass than the other fixatives and that these polymers aggregate particles via a "bridging" mechanism (*27*). The increase in larger particle growth can be thus attributed to aggregation by the longer cPAM chains bridging the particles.

FixA (pDADMAC) showed very little growth in both the smaller colloidal and larger particle size. The higher molar mass pDADMAC fixatives (FixB, FixC) as well as the pDADMAC co-polymer fixatives (FixH and FixI) showed little to no effect on the colloidal particle size but all affected the larger particle size growth.

The addition of FixJ (pAC) was found to increase colloidal particle size but only have a small effect on large particle size growth. It is possible that though the colloidal particles are larger, than those of most fixatives, they are still stable with pAC at 4.75 pH.

At 4.75 pH, particle size after a dose of 2.0 kg 'as received' fixative per tonne of oven dried. TMP can reach up to 8 µm in diameter from an untreated starting size of approximately 0.3 µm in diameter, as shown in Figure 6. The majority of fixatives however do not increase large particle size above 2.5 µm. FixF (pAM), FixI (p(AM-co-DADMAC)), FixL (pEI) and FixM (pEI) increase large particle size to 3-4 µm while FixD and FixE (both pAM) increase large particle size to greater than 6 µm. It is uncertain whether these larger particles are aggregates or agglomerates, in either case there is a concern that the

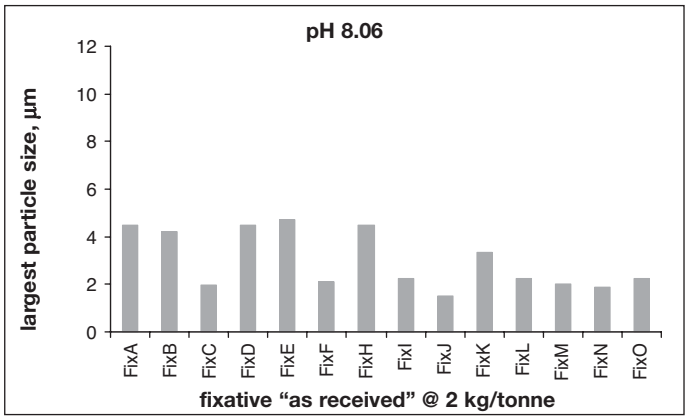


Fig. 10 Largest particle size (µm) at 8.06 pH.

larger particles result in greater risk of pitch deposition due to destabilisation (e.g. pH shock, shear forces, etc.) or further agglomeration of these large particles.

At 6.85 pH, FixE (pAM) had the highest growth rate in colloidal size and the highest growth rate in larger particle size as shown in Figure 7. FixG (*guar gum*) had the slowest growth rate of larger particle size. FixH (p(AM-*co*-DADMAC)) showed large particle size growth at 6.85 pH but not at 4.75 pH.

The majority of fixatives did not increase large particle size above ~4.5 µm, at 6.85 pH as shown in Figure 8. As at 4.75 pH (Fig. 6), increased the large particle size to the greatest extent, producing particles larger than 9 µm in diameter. FixH (p(AM-*co*-DADMAC)) increased large particle size to ~7 µm.

At 8.06 pH, FixD and FixE, both pAM fixatives, lead to a decrease in colloidal size and a rapid increase in larger particle size through aggregation as shown in Figure 9. FixH (p(AM-*co*-DADMAC)) was found to cause a rapid increase in colloidal particle size and a growth of large particle size though less than that of FixD and FixE. FixB and FixA (both pDADMAC) as well as FixF (pAM) increased the colloidal particle size at 8.06 pH though not as sharply as FixH (p(AM-*co*-DADMAC)).

In general, the extent of particle size growth was lower at 8.06 pH when compared to the particle size growth at 6.85 pH. Similarly the effect of pAM (FixD, FixE & FixF) on particle size growth was not as great at 8.06 pH as at 6.85 pH. These observations would suggest that as the cationic charge of the fixatives decreases with increasing pH so does the ability to agglomerate larger particles.

Of the three pH values studied 8.06 pH had the smallest large particles with none of the fixatives increasing the large particle size above ~4.5µm (Fig. 10). Half of the fixatives studied did not increase large particle size above 2.5µm.

CONCLUSIONS

The fixatives studied generally fall into two categories – colloid disrupting and colloid stabilising:

1. The first category of fixative disrupts colloidal stability and leads to the formation of larger particles (i.e. >2 µm).
2. The second category of fixative either does not affect, or has a positive effect on, colloidal stability. Some of the fixatives in this category also show little growth in larger particles (i.e. >2 µm).

Table 3 shows the fixatives placed into these two categories at each pH based on the LPSA results obtained.

FixD and FixE (both pAM) are categorised as colloidal disrupting at all pH values, whereas FixC (pDADMAC), Fix G (guar gum), FixJ (pAC) FixN and FixO (both pVAm) are categorised as stabilising colloids at all pH values. In the case of FixC and FixJ the stabilisation is believed to be due to the uniformity of the charged unit spacing within the polymer backbone. It is likely that FixD and FixE destabilise colloids through flocculation and polymer bridging (*27*) as these fixatives have 2-3 times higher molar mass than the other fixatives studied.

The demarcation between the two classifications is not clear for some types of fixatives. Other factors such as molar mass and charge density appear to also influence the mechanism by which the fixative interacts with the pitch particles. At lower pH the pDADMACs (FixA, FixB & FixC) tend to stabilise colloids, but as pH increases the lower molar mass pDADMACs start to disrupt colloidal stability. It is possible that as pH increases, larger 'patches' (*28*) of higher molar mass pDADMAC are needed to neutralise the higher negative charge of the colloids in order to stabilise the colloids.

Table 3
Fixative categories as determined by LPSA.

pH	Colloid disrupting fixatives	Colloid stabilising fixatives
4.75	FixD, FixE	FixC, FixH, FixK, FixN, FixO,
	Maybe: FixF, FixI, FixL, FixM	Maybe: FixJ, FixA, FixB
6.85	FixD, FixE, FixH	FixB, FixC, FixL, FixO, FixG
	Maybe: FixA, FixF, FixK	Maybe: FixJ, FixM, FixN
8.06	FixA, FixB, FixD, FixE, FixH, FixK	FixC, FixJ, FixG
		Maybe FixF, FixI, FixL, FixM, FixN, FixO

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REFERENCES

(*1*) Wågberg, L. and Ödberg, L – The action of cationic polyelectrolytes used for the fixation of dissolved and colloidal substances. *Nordic Pulp and Paper Res. J.* **6**(3):127-135(1991).

(*2*) Shetty, C.S., Greer, C.S., and Laubach, G.D – A Likely Mechanism for Pitch Deposition Control. *TAPPI J.* **77**(10):91-96(1994).

(*3*) Blomquist, M – Fast and convenient methods for characterization of pitch deposits and pitch deposition tendency. *Report. Åbo Akademi University, Assignment from Ph.D. Course "Fundamental Chemistry of Pulp and Papermaking Analytical Methods"*. (2003).

(*4*) Allen, L.H. – Chapter 13 - Pitch Control in Paper Mills, In Back, E.L. and Allen, L.H., (eds.) **Pitch Control, Wood Resin and Deresination**, TAPPI Press: Atlanta. 307-328(2000)

(*5*) Richardson, D. and Grubb, M. – Extractives removal from Newsprint Mill process waters by Dissolved Air Flotation, *58th Appita Ann. Gen. Conf. Proc.,* Canberra, Australia. p. 79-84(2004)

(*6*) Maher, L.E., Stack, K.R., McLean, D.S., and Richardson, D.E. – Adsorption behaviour of cationic fixatives and their effect on pitch deposition, *59th Appita Ann. Gen. Conf. Proc.,* Auckland, New Zealand p.115-122(2005)

(*7*) Hassler, T. – Pitch deposition in papermaking and the function of pitch-control agents, *TAPPI J.* **71**(6),195-201(1988).

(*8*) Dreisbach, D.D. and Michalopoulos, D.L. – Understanding the behavior of pitch in pulp and paper mills, *TAPPI J*. **72**(6):129-134(1989).

(*9*) McLean, D.S., Breadmore, M.C., Stack, K.R., Richardson, D.E., and Haddad, P.R. – Wood pitch fixative selection by capillary electrophoresis, *59th Appita Ann. Gen. Conf. Proc*. Auckland, New Zealand. p. 137-141(2005)

(*10*) Allen, L.H. – Pitch particle concentration: an important parameter in pitch problems, *Transactions*, CPPA. **3**(2):TR32-TR40(1977).

(*11*) Garver, T.M. and Yuan, H. – Measuring the response of pitch control strategies, *Pulp and Paper Canada*. **103**(9):24-28(2002).

(*12*) McLean, D.S. – The Effect of Wood Extractive Composition on Pitch Deposition. **MSc Thesis**, School of Chemistry. Hobart: University of Tasmania. (2003).

(*13*) Barth, H.G. and Sun, S.-T. – Particle Size Analysis, *Analytical Chemistry*. 63(12): 1R-10R(1991).

(*14*) Barth, H.G. and Sun, S.-T. – Particle Size Analysis, *Analytical Chemistry*. **65**(12):55R-66R(1993).

(*15*) Rayleigh, L.- On the Electromagnetic Theory of Light, *The London, Edinburgh, and Dublin Philosophical Mag. and J. Sci*. **12**(73):81-101(1881).

(16) Fraunhofer, J. – Bestimmung des Brechungs- und des Farbenzerstreungs-Vermögens verschiedener Glasarten, in Bezug auf die Vervollkommnung achromatischer Fernröhre. *Annalen der Physik*. **56**:264-313(1817).

(*17*) Mie, G. – Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen,Annalen der Physik. **3**(25):377-445(1908).

(*18*) Wedd, M.W. – Determination of Particle Size Distributions Using Laser Diffraction. *Educational Resources for Particle Technology*. **4**(1):1-4(2003).

(*19*) Eshel, G., Levy, G.J., Mingelgrin, U., and Singer, M.J. – Critical Evaluation of the Use of Laser Diffraction for Particle-Size Distribution Analysis. *Soil Sci. Soc. America J*.. **68**(3):736-743(2004).

(*20*) Kröhl, T., Lorencak, P., Gierulski, A., Eipel, H., and Horn, D. – A new laser-optical method for counting colloidally dispersed pitch, *Nord. Pulp Pap. Res. J*. **9**(1):26-30, 36(1994).

(*21*) Yu, L., Allen, L.H., and Esser, A. – Evaluation of a laser-optical resin particle counter, *J. Pulp and Paper Sci*. **29**(8):260-266(2003).

(*22*) Belouadi, C., Blum, R., and Esser, A. – A Novel Approach to Avoiding White Pitch Deposition, *Pulp and Paper Canada*. **101**(9):254 - 257(2000).

(*23*) Yu, L., Allen, L.H., and Esser, A. – Evaluation of a laser-optical resin particle counter , *TAPPI J*. **2**(3):13-18(2003).

(*24*) Maher, L. – Cationic fixatives: Adsorption behaviour and effect on pitch deposition. **BSc Hons Thesis.** School of Chemistry. Hobart: University of Tasmania. (2004).

(*25*) Dechandt, A., Watkins, T., and Pruszynski, P. – Total approach to deposit Control on Newsprint machine using TMP and DIP pulp mix - from specialized fixation of individual pulps to retention, *Appita J*. **57**(1):13-18(2004).

(*26*) McLean, D.S., Stack, K.R., and Richardson, D.E. – The effect of wood extractives composition, pH and temperature on pitch deposition. *Appita J*. **58**(1):52-55, 76(2005).

(*27*) Pelssers, E.G.M., Stuart, M.A.C and Fleer, G.J. – Kinetic Aspects of Polymer Bridging: Equilibrium Flocculation and Nonequilibrium Flocculation. *Colloids and Surfaces*, 38:15-25 (1989).

(*28*) Tripattharanan, T., Hubbe, M.A., Heitmann, J. A and Venditti, R.A. – Effect of idealised flow conditions on retention aid performance. Part 2: polymer bridging, charged patches, and charge neutralisation. *Appita J.,* **57**(6):448-454 (2004).

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